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Fabrication of Graphene on Kevlar Supercapacitor Electrodes

by Jacquelyn M. Krintz and Matthew H. Ervin

ARL-TR-5545 **May 2011**

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14. ABSTRACT

Wearable electronics have become a growing topic of interest for the application of energy storage devices. Supercapacitors have high energy densities compared to conventional capacitors, making them desirable for military applications. Supercapacitors have been fabricated with graphene to investigate its applicability for energy storage devices, as this carbon-based material has a large surface area and mechanical/chemical stability. In this study, we investigate the potential of graphene electrodes on Kevlar supports created using a dip-and-dry technique. This report demonstrates how applying different masses of graphene affects the specific capacitance of the Kevlar-supported graphene electrodes.

15. SUBJECT TERMS

graphene, supercapacitor, Kevlar, electrochemical capacitor

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1. Background

Soldier protection has undergone significant advances in technology over the decades. One protective material, Kevlar, is a well-known material used in the field to protect Soldiers from gunfire and explosive debris. Recent studies on Kevlar have been explored to make it more flame-resistant and cut-resistant; studies have also sought to produce electronic textile out of Kevlar for the transport of data and power (*1–3*). Wearable electronics has become a growing topic of interest for the application of energy storage devices, including supercapacitors. Supercapacitors have high energy densities and can carry the same amount of energy in a smaller volume compared to conventional capacitors, making them potentially attractive for military applications.

Supercapacitors have been fabricated with graphene to investigate this carbon-based compound for use in energy storage devices because of its mechanical and chemical stability (*4*). Graphene is a one-atom-thick, 2-dimensional compound (*5*), which allows for flexible movement, making feasible applications such as wearable electronics. Graphene's high surface area—all the atoms are surface atoms—could also be used to generate large capacitance.

In this study, graphene is investigated for use in supercapacitor electrodes. This can potentially increase a supercapacitor's energy density, which is needed for sufficient energy storage for many applications. To investigate the potential of graphene electrodes, Kevlar-supported graphene electrodes were created in order to explore the energy density achievable and to demonstrate flexible fabric-based supercapacitor electrodes.

2. Motivation

The purpose of this research is to investigate the feasibility of creating a ballistic protection energy storage device composed of Kevlar material and graphene. Combining ballistic protection and energy storage in one system could reduce the amount of weight Soldiers carry in the field, making these innovative energy storage devices useful for Army applications.

3. Experimental Setup and Calculations

3.1 Materials

Two different flexible Kevlar-based materials were used for electrode supports in this experiment:

- Kevlar cloth
- Aracon® brand metal clad Kevlar fiber (Mirco-Coax®)

Before graphene oxide application, the conductivity of the fibers was measured using a multimeter.

3.2 Graphene Oxide Application

A stock solution of graphene oxide (GO), obtained from Cheaptubes.com, was used that had a concentration of 2 mg/mL. A dip-and-dry technique (*6*) was performed to cover the Kevlar-based susbstrates with 1 mL aliquots of GO. Figure 1 shows an example of applying GO to the fibers.

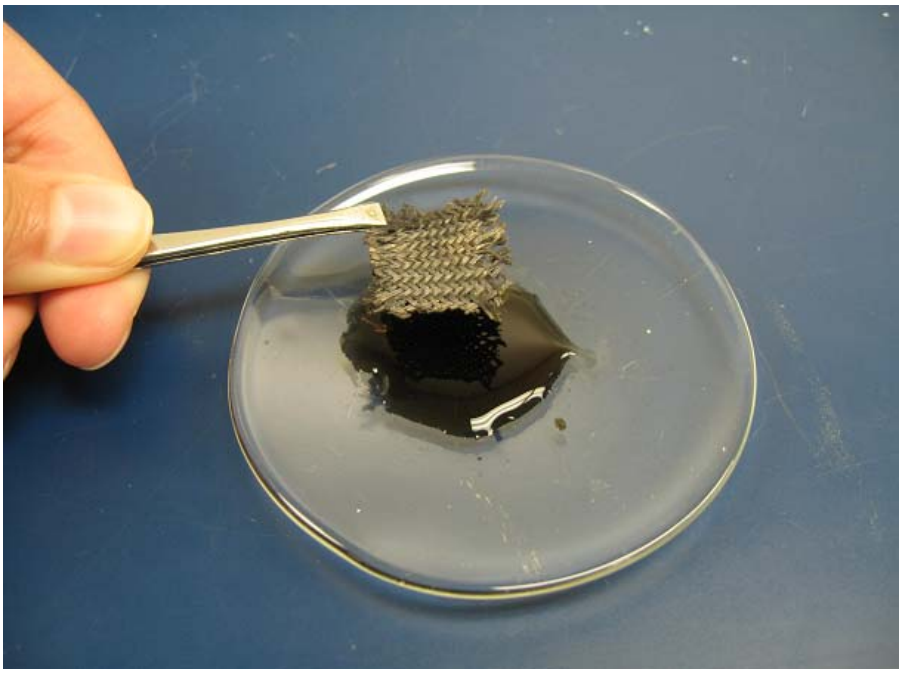

Figure 1. Dip-and-dry technique applied to Kevlar-based electrodes.

The wetted fibers were dried on a hotplate at 125 °C before continuing the coating. Once the coated fibers were dried, the GO was thermally reduced by placing the electrode on a hotplate at 200 °C overnight. Conductivity measurements were taken after GO reduction to see if conductivity improved or worsened.

3.3 Preparing dilute graphene oxide

A series of dilutions of the GO solution were prepared using methanol as the solvent. We found that methanol was a better solvent than water because it helped the GO penetrate between the Kevlar fibers and reduced the amount of flaking. Dilutions of 3:1, 5:3, 50:50, 1:2, 1:3, 1:5, 1:10, and 1:20 GO:methanol were prepared and used for depositing different masses of GO.

3.4 Characterization of graphene-coated Kevlar fibers

The reduced GO electrodes were wrapped with nickel (Ni) wire to make electrical contact for cyclic voltammetry (CV) testing. A VersaSTAT 3, Princeton Applied Research electrochemical workstation was used. The cyclic voltamograms for graphene electrodes made with the Kevlar fibers were measured between 0.3 V to –0.7 V, and those made with the metal-clad Kevlar fibers were measured between 0.2 V to –0.35 V. The metal-clad fibers were tested with a narrower potential range because these electrodes exhibited reduction-oxidation peaks from the copper metal present in the metallization, which was deposited onto these fibers using an electroless plating process. A larger potential swing between 0.3 V to –0.7 V would incorporate these redox peaks. All CV scans were performed at a scan rate of 0.02 V/s in an electrolyte of 1 M potassium hydroxide (KOH) solution. A three-electrode system was set up for the CVs, as shown in figure 2.

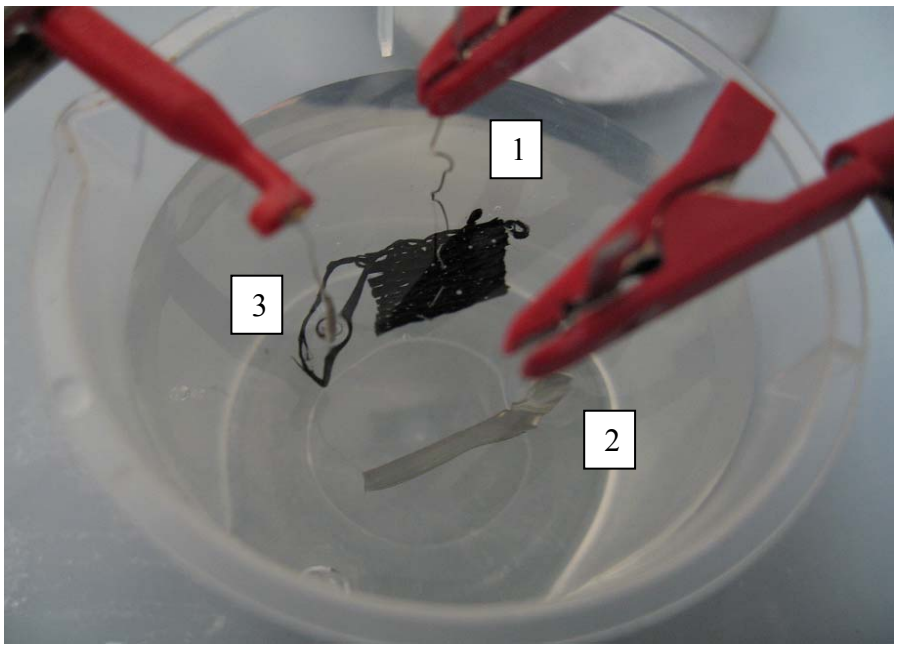

Figure 2. Three-electrode system used for the CV measurements. The (1) working electrode was the Kevlar-based electrode; (2) the counter electrode was nickel foil and (3) the reference electrode was a Ag/AgCl pellet electrode.

Equation 1 was used to calculate the capacitance:

$$\text{Capacitance (F)} = \text{current (A)} / \text{scan rate (V/s)}, \quad (1)$$

where capacitance is in farads, F, current is in amps, and the scan rate is in volts per second. Equation 2 was used to calculate the specific capacitance, C_s:

$$C_s\ (\text{F/g}) = \text{capacitance (F)} / \text{mass of graphene (g)}, \quad (2)$$

where specific C_s is in F/g, and mass of graphene is in grams. The mass is calculated from the GO solution concentration and the volume applied to each electrode. When GO is thermally reduced, mass is lost due to the loss of oxygen, but the weight of the resulting G is unknown since the stoichiometry of the GO is unknown. Therefore, the mass of the original GO is used here to calculate the specific capacitance.

4. Results and Discussion

We first experimented with Kevlar fiber bundles and graphene. Low capacitance—between 0.005 and 0.02 F/g—was obtained from CV testing of these electrodes. The Kevlar fiber bundles alone had no conductivity. Coating the Kevlar with graphene did not improve the conductivity sufficiently; therefore, we needed to create a better current-collecting substrate. Carbon fibers were integrated into the Kevlar fiber bundles, which helped the conductivity of the electrode. Applying graphene further improved the capacitance of these electrodes, but we found that the graphene-coated Kevlar fibers were not contributing to the improved capacitance seen in the CV measurements, which was equal to that of the graphene-coated carbon fibers only.

We then switched to using Ni-coated Kevlar braid as an electrode support and current collector, since the Ni coating greatly improves the conductivity of the Kevlar fabric and, therefore, the capacitance of the resulting graphene electrodes. Using Aracon® brand metal-clad Kevlar fiber, we applied several aliquots of graphene to the electrode. This Kevlar fiber is not a ballistic-proof fiber, but it is chemically similar. These metal-clad Kevlar braids had a resistance of approximately 0.4Ω for a 1.4-cm length of braid. Figure 3 shows an example of graphene-coated Kevlar supercapacitor electrodes observed using a scanning electron microscope (SEM). Table 1 shows the capacitance and specific capacitance results obtained using different masses of graphene applied to 1.4-cm long pieces of Ni-coated Kevlar braid (which have a total fiber surface area of approximately 5.6×10^{-3} m^2, calculated using a fiber diameter of 22 microns, 180 fibers per tow, and 32 tow per braid).

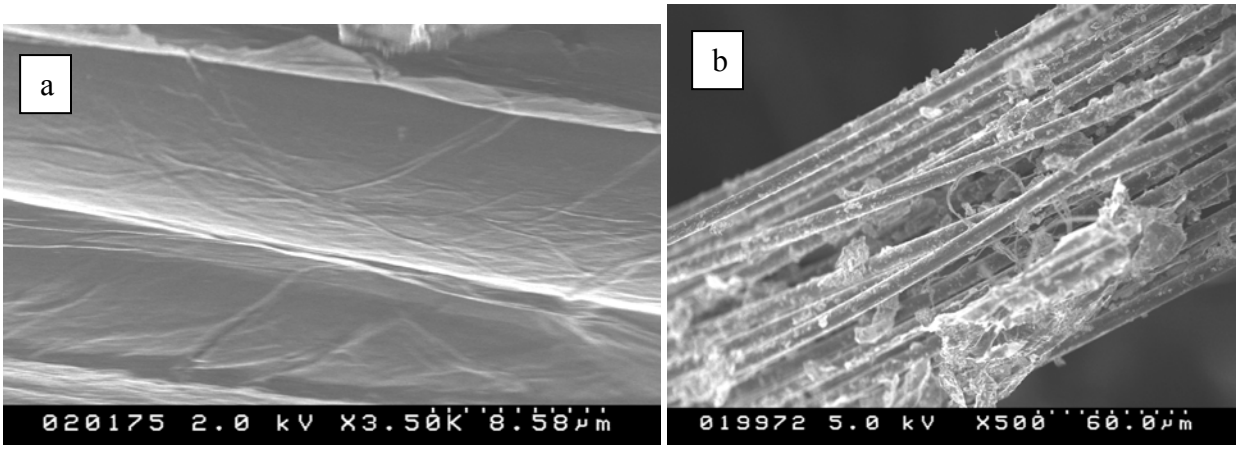

Figure 3. Graphene coated Kevlar fibers. (a) The wrinkles on the individual fibers are from the graphene coating. (b) A lower magnification of graphene coated fibers is shown.

Table 1. Various masses of graphene applied to Aracon® brand metal clad fiber using water based solutions.

Electrode	Graphene Solution*	Mass of graphene (mg)	Capacitance (mF)	Specific Capacitance (F/g)
1	1:10	0.346	6.3	18.1
		0.72	17.5	24.3
		1.44	10.6	7.4
2	1:1	1.0	10.0	10.0
		2.0	24.8	12.4
3	5:3	1.25	18.8	15.0
		2.5	47.5	19.0
4	5:2	1.43	23.8	16.5
		2.86	25.0	8.7

*solution of graphene with water as the solvent

The results show that while the capacitance did tend to improve with additional application of graphene, at a certain point it would drop off. This was due to the graphene flaking off of the fibers. The water-based graphene solutions did not wet the Kevlar well enough to thoroughly penetrate the fibers, thus the deposited graphene was only sitting on the surface of the electrode; there came a point when this layer of graphene was no longer making good contact with the substrate, as verified by a decrease in the measured electrode conductivity. SEM images, shown in figure 4, also show evidence of graphene flaking off of these electrodes.

A solvent other than water was needed to alleviate this flaking problem; methanol, therefore, was added to the water-based solution. The added methanol reduced the solution surface tension enabling the graphene to more fully penetrate into the fibers of the electrode. A further study of graphene electrodes made using the methanol-containing solutions was performed using

Aracon® brand metal-clad fiber substrates. Table 2 lists the different masses of graphene deposited with their resulting capacitances and specific capacitances. Specific capacitances were observed to increase with smaller masses of graphene. This is likely due to the easier accessibility of the graphene surface area in a thinner deposit, as well as a reduced resistance due to the graphene film. In these calculations, the capacitance due to the Ni metal-coated Kevlar alone was subtracted to avoid a systematic error that would also tend to make the specific capacitance increase at lower graphene masses (e.g., with no graphene, there would still be capacitance due to the Ni-coated Kevlar that would result in an infinite graphene specific capacitance calculated).

There is also a jump in the capacitance between the graphene film masses of 1.50 mg to 1.25 mg where the capacitance starts low (~20–15 mF) then increases ~36–37 mF, respectively, before the capacitance continues to decrease with decreasing graphene mass on the electrodes. The low capacitance for the 1.50 mg film could again be due to the graphene film being too thick, resulting in flaking or poor electronic or ionic conductivity.

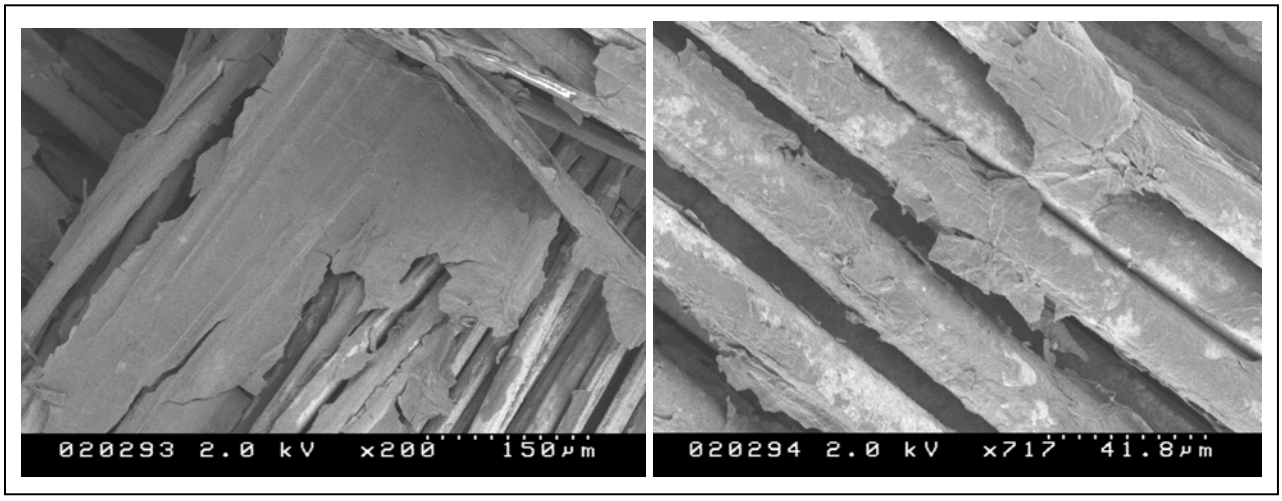

Figure 4. SEM images of flakes of graphene on metal-clad Kevlar fibers. This graphene was deposited with a water based solution.

Table 2. Mass of graphene on Aracon® brand metal clad fiber and their corresponding capacitance and specific capacitance. A one mL aliquot of a suitably diluted solution was used for each electrode.

Electrode	Mass of Graphene (g)	Run 1 Capacitance (mF)	Run 2 Capacitance (mF)	Run 1 Specific Capacitance (F/g)	Run 2 Specific Capacitance (F/g)
1	1.50	20.0	15.7	13.3	10.4
2	1.25	37.5	36.9	30.0	29.5
3	1.00	25.0	31.3	25.0	31.3
4	0.67	27.5	30.3	41.0	45.1
5	0.50	26.3	22.5	52.5	32.5
6	0.33	24.8	21.3	75.2	64
7	0.18	15.0	13.8	82.4	75.5
8	0.10	11.9	11.3	125.0	118.4

Figure 5 shows a typical cyclic voltamogram from a graphene on Kevlar electrode. The difference in current between the oxidation (upper) and reduction (lower) sides of the curve, at zero volts, is divided by two to obtain the current for calculating the capacitance using formula 1. As is shown in table 2, higher amounts of graphene resulted in larger amounts of capacitance, except for the highest mass used where flaking was probably an issue. However, larger specific capacitance is achieved with lower masses of graphene (see table 2), due to improved ionic and electronic conduction through thinner films. Figure 6 graphically shows the trend of increasing C_s as the mass of the graphene decreases. Duplicate runs of the same masses of graphene were performed in order to demonstrate reproducibility.

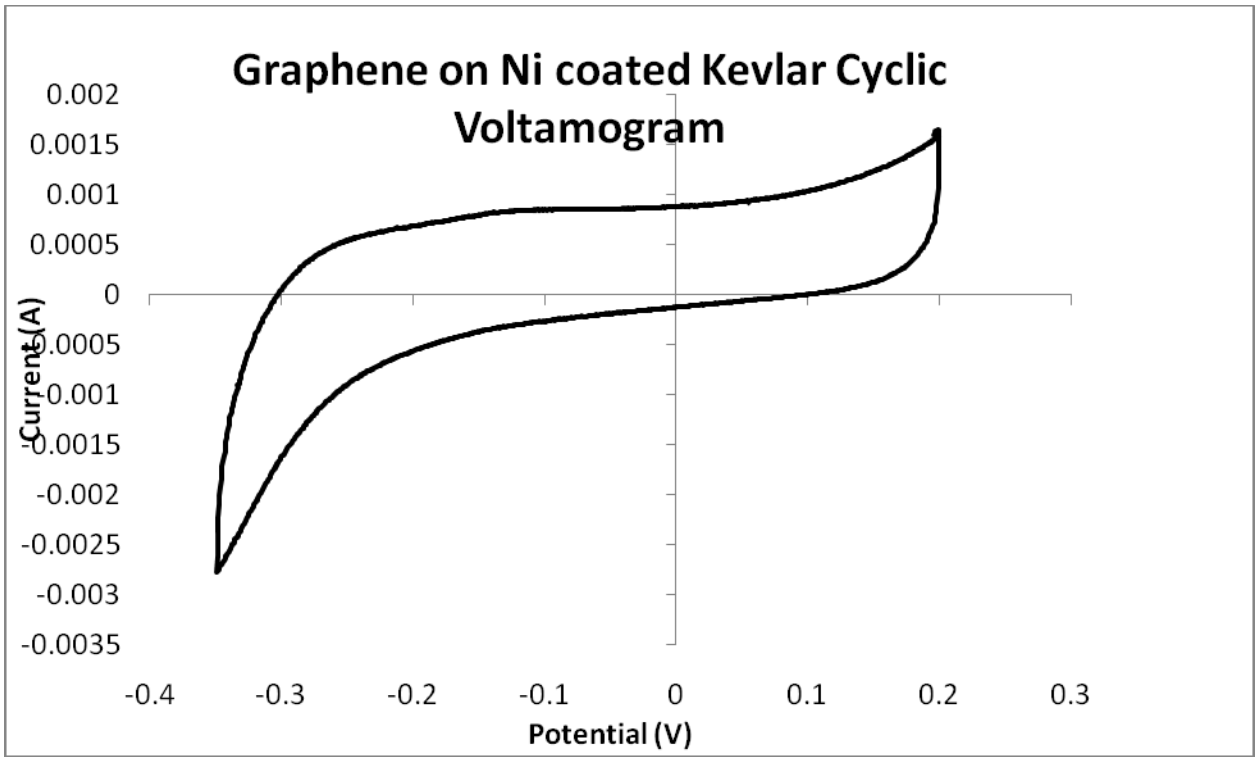

Figure 5. Typical CV scans for graphene coated Aracon® brand metal clad Kevlar fiber.

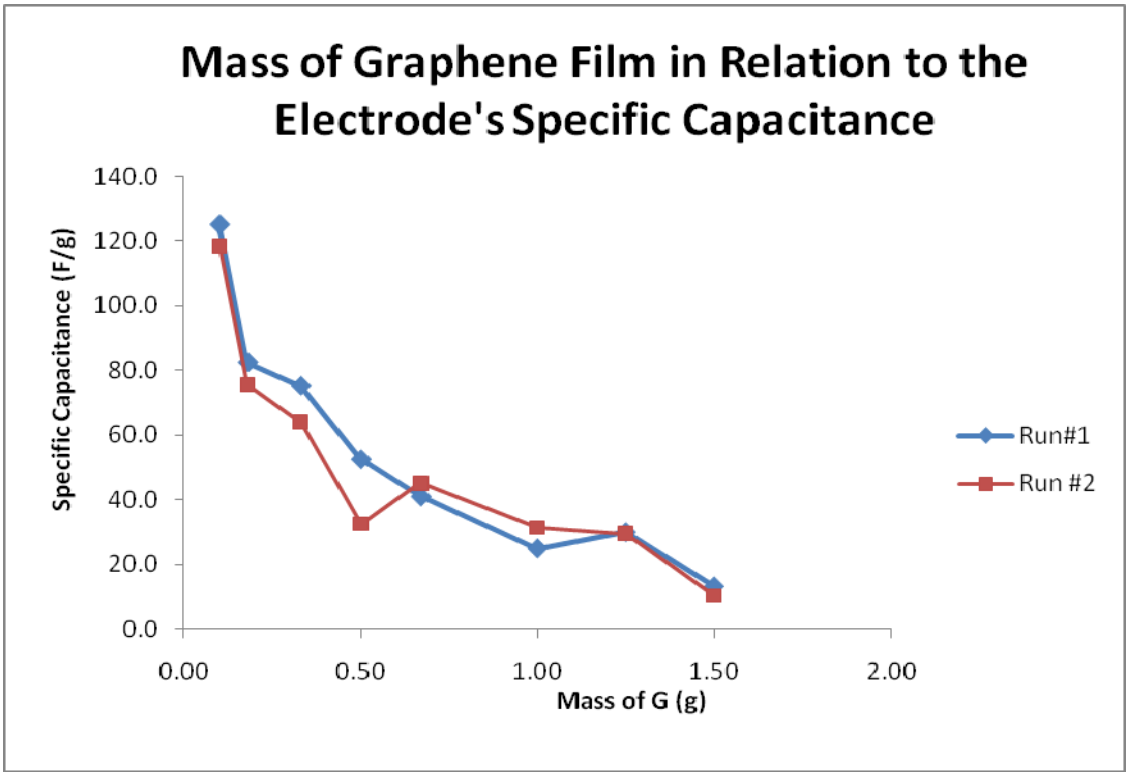

Figure 6. Mass of graphene film in relation to electrode's specific capacitance on Aracon® brand metal clad fiber.

A Ragone plot, shown in figure 7, was constructed to display electrode energy densities versus power densities. Electrodes with graphene films of 1.50 mg, 0.50 mg, and 0.095 mg were measured. We found that the electrode with a graphene film of 0.095 mg had the highest energy density, as well as power density (calculated using only the mass of the graphene). The electrode with the lowest energy and power density was the 1.5 mg film. This trend is not surprising, as we have already seen that the specific capacitance increases with lower mass deposits, presumably due to higher electronic and ionic conduction through thinner films.

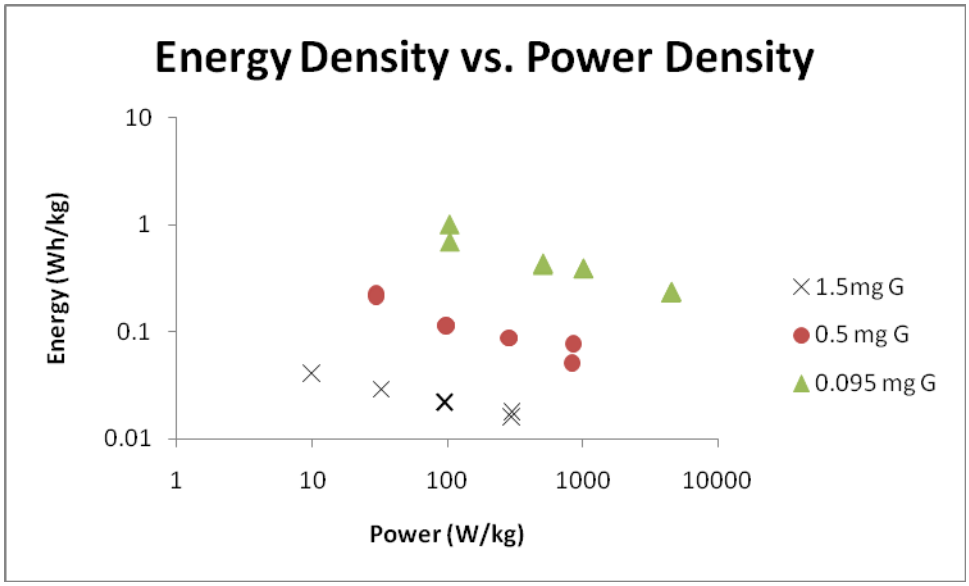

Figure 7. Ragone plot of energy density versus power density for different masses of G on Aracon® brand metal-clad fiber.

Figure 8 shows electrode capacitance as a function of current density. We can see, looking at the three plots, that as current per gram is lowered, higher capacitance is reached. This is due to the ionic resistance in the electrodes (the resistance to the diffusion of ions through the pores of the electrode). The electrode can be thought of as a distributed capacitance and resistance (transmission line behavior), where there is additional resistance experienced for the additional capacitance due to a thicker graphene layer. This results in capacitance contributions with differing time constants, such that at high charging/discharging rates only a subset of the capacitance is participating.

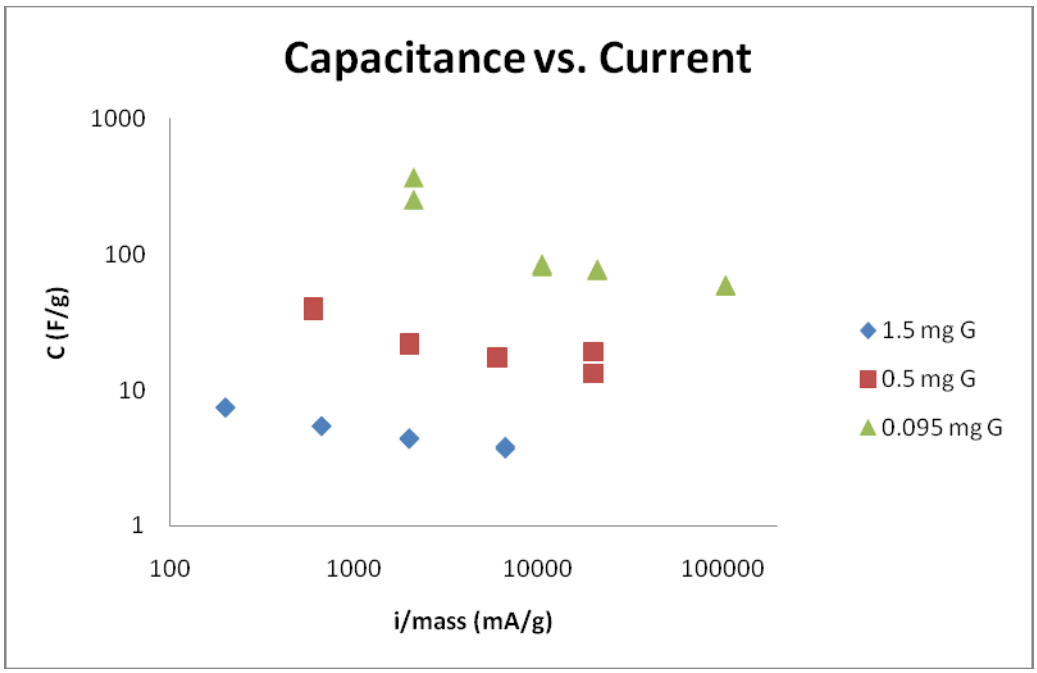

Figure 8. Specific capacitance as a function of current density for each electrode tested. The electrode containing 0.095 mg of graphene yielded greater specific capacitance.

5. Conclusions

The beginnings of this work were to develop a Kevlar-supported graphene electrode that would be able to achieve useful amounts of capacitance. We found that bare Kevlar fibers were not an adequate support for these graphene-based electrodes, as a conductive current collector was also needed since the graphene coating was not sufficiently conductive to function as a good current collector. Therefore, we switched to metalized-Kevlar fibers. These proved to have good conductivity and produced better results. An experiment to see if capacitance would increase with increasing graphene coating onto the fibers showed that the graphene would begin to flake off due to excessively thick graphene, in part due to poor penetration of the graphene and water solution into the fibers. A solvent other than water was needed to better wet the fibers in order to alleviate the issue of flaking. Methanol was found to lower the surface tension of the graphene solutions and resulted in more uniform coverage of the fiber substrates. Different masses of graphene applied to these metalized fibers were investigated, and lower amounts of graphene were found to produce larger specific capacitance. In addition, the thinner graphene electrodes yielded greater power and energy densities (calculated based on the mass of the graphene alone).

In a real device, the mass of the Kevlar, electrolyte, and packaging will contribute to the packaged-device energy and power density so that the optimum graphene mass density on the fibers will depend on all of the parameters of the final packaged device. Future work on these devices will focus on ensuring that the full thickness of Kevlar fabric is evenly coated with graphene, tuning the porosity of the deposited graphene film to optimize surface area, and possible incorporation of pseudocapacitance to increase energy density.

6. References

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List of Symbols, Acronyms, and Abbreviations

Ω	ohm
A	amps
Ag/AgCl	silver/silver chloride
CV	cyclic voltammetry
C_s	specific capacitance
F/g	Farads per gram
GO	graphene oxide
KOH	potassium hydroxide
MeOH	methanol
mF	milliFarads
mg/mL	milligrams per milliliter
Ni	nickel
SEM	scanning electron microscope
V	volts
V/s	volts per second

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